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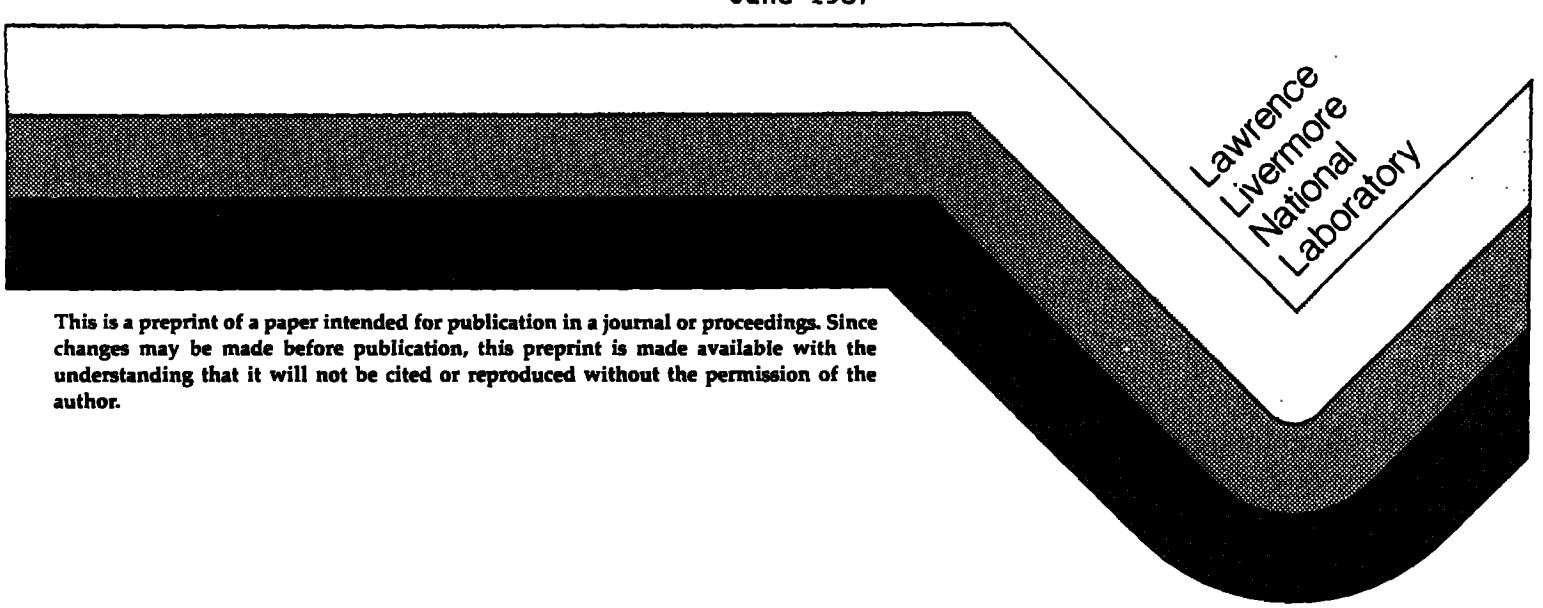

DISCLAIMER

OPTICAL PROPERTIES OF CR^{3+} IN FLUORIDE HOSTS*

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We will present information which suggests that the lattice relaxation around a Cr^{3+} impurity must be accounted for when interpreting the optical spectra of the ion. Special attention is given to fluoride lattices in which the cation radius is larger than that of Cr^{3+}.

1. INTRODUCTION

The understanding of the properties of transition metal ion impurities in insulating hosts is based upon the concept that the crystal environment modifies the $3d^n$ energy levels of the free-ion.[1] Thus, one initially needs to have information concerning the properties of the ion in free space, and also about the nature of the host site into which the ion, (Cr^{3+}, in this case), is to be incorporated. Here, we note that there are two important aspects of the crystal site: the identity of the nearest-neighbor (n.n.) anions, and the size of the host metal ion that is to be replaced. The dependence of the magnitude of the crystal field splitting, Dq, on the particular n.n. anion has long been rationalized in terms of the spectrochemical series. The influence of the size of the site, on the other hand, might be understood in terms of the simple electrostatic model of crystal field theory. In this article, we will show, however, that the lattice relaxation around the Cr^{3+} ion is a particularly important effect that needs to be considered.

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2. RESULTS AND DISCUSSION

2.1 Spectroscopy of Cr^{3+} in CdF_2, CaF_2, SrF_2 and BaF_2

The cation site of fluorite-structure hosts is normally eightfold coordinated, although the rather large difference in ionic radius of the host and Cr^{3+} ions (e.g. 1.1Å for Ca^{2+} versus 0.6Å for Cr^{3+}) assures that some degree of lattice relaxation will take place. In fact, the optical spectra as well as previously reported EPR results[2] indicate that the Cr^{3+} site becomes coordinated by six of the eight fluorines.

The absorption and emission spectra of Cr^{3+} in CdF_2, CaF_2, SrF_2 and BaF_2 are shown in Fig. 1.[3] In agreement with the predictions of the d^3 Tanabe-Sugano diagram in octahedral symmetry, the energies of the $^4A_2 \rightarrow {}^2E$ and $^2T_1$ transitions do not change with host lattice, while the transition energies to the $^4T_2$ and $^4T_1$ states do vary somewhat due to differences of the crystal field strength of the various hosts. We cannot account for the absorption bands if it is assumed that the Cr^{3+} ions are in eightfold coordination. In Fig. 2 we illustrate the likely mechanism by which the lattice relaxation in the fluorite-structure hosts would produce sixfold coordination.[3]

2.2 Spectra of Cr^{3+} in other fluoride hosts

As discussed above, the Cr^{3+} impurity substantially modifies the fluorine positions of the fluorite-structure hosts. If this effect were of a general nature, we would expect to also observe it in crystals having natural octahedral sites. Referring to Table 1, we see that values of Dq for K_2NaCrF_6 and $K_2NaScF_6:Cr^{3+}$ are nearly the same, despite the larger Sc site.[4] The CrF_3 and $ScF_3:Cr^{3+}$ systems show a similar

trend. This must mean sufficient relaxation of the n.n. fluorines occurs at the impurity sites so as to result in a n.n. environment that is similar to that of the pure Cr^{3+} compounds.

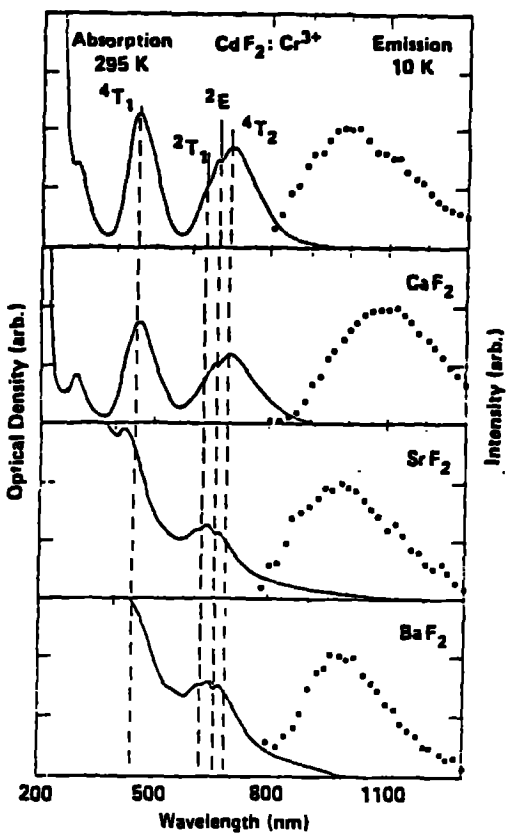

FIGURE 1. Absorption and emission spectra of Cr^{3+} in four fluorite-structure hosts. The final states for absorption are indicated for CdF_2.

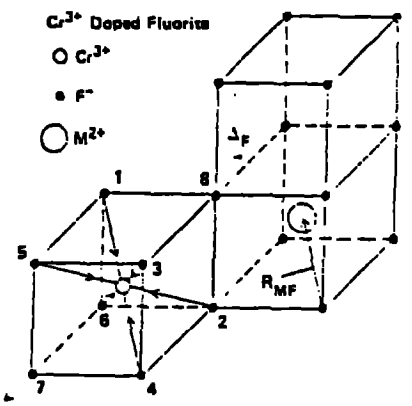

FIGURE 2. Pictorial representation of the relaxation of a ground state Cr^{3+} site.

TABLE 1
Comparison of Sc-containing fluoride crystals
with pure Cr^{3+} compounds at 300K

Crystal	Dq(cm^{-1})	Metal-Anion Distance (Å)
K_2NaCrF_6	1610	1.93
K_2NaScF_6	1560	1.99
CrF_3	1460	1.90
$ScF_3:Cr^{3+}$	1410	2.01

3. CONCLUSIONS

We have found that the net effect of the lattice relaxation is to result in n.n. environments and optical spectra that are more similar than otherwise expected.

ACKNOWLEDGEMENTS

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